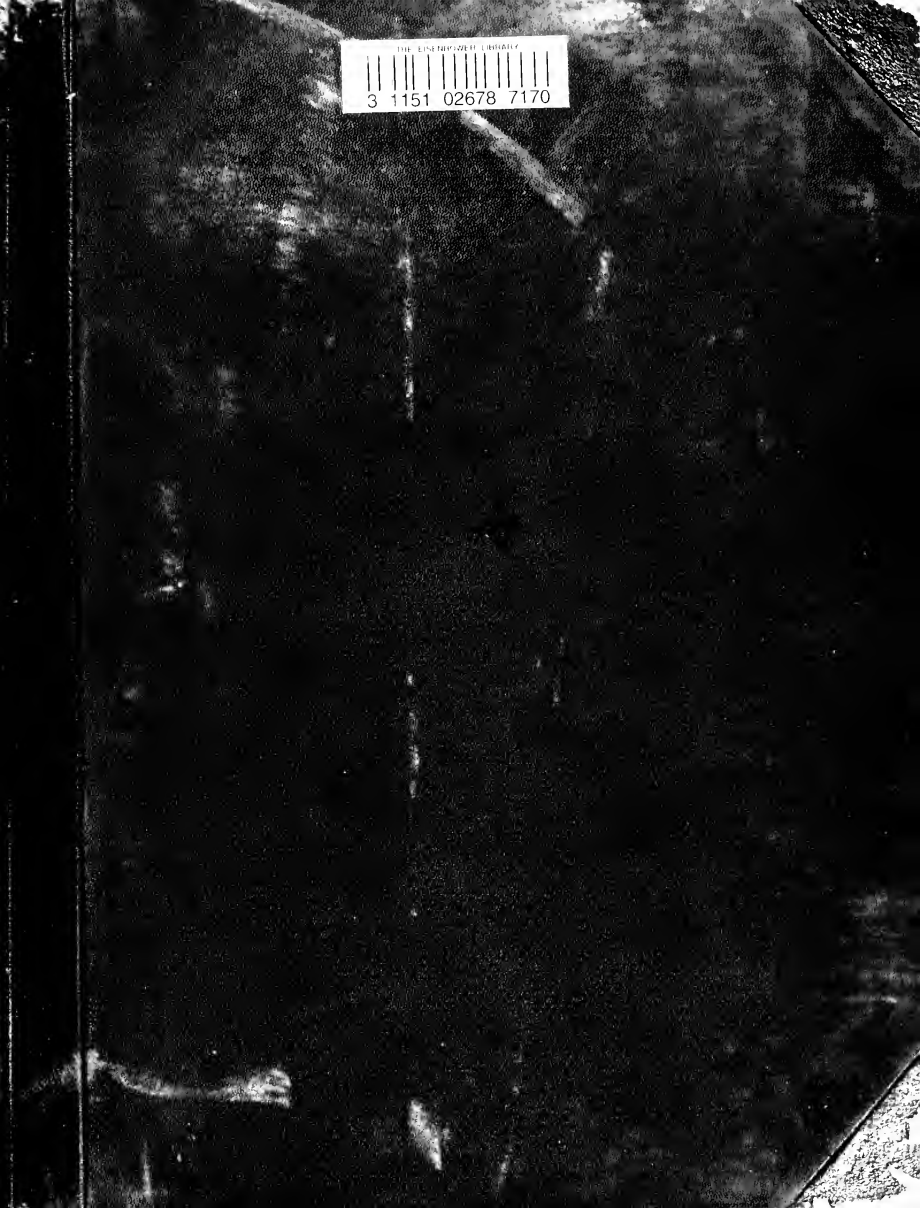
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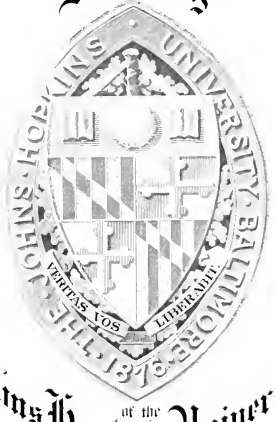

of the
Johns Hopkins University

# THE RELATION OF THE ANILIDES -A-

OF

ORTHOSULPHOBENZOIC ACID.

Dissertation

Submitted to the Board of University Studies of the

Johns Hopkins University for the Degree

of Doctor of Philosophy

by

JOSEPH RUFUS HUNTER.

1893.

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The investigation described in the following pages was undertaken at the suggestion of Professor Ira Remsen, and carried on under his constant supervision. I gladly avail myself of this opportunity to express to him, as well as to Professor H. N. Morse, my sincere gratitude for the assistance they have freely rendered me during its progress.

## I. INTRODUCTION.

Ortho-sulphobenzoic acid was first prepared by Remsen and Fahlberg (1) in the year 1879, by oxidizing ortho-toluene sulphonamide by potassium permanganate in alkaline solution. It was further investigated by Remsen and Dohme (2) who prepared a large number of its salts, as well as its chloride obtained by the action of phosphorus pentachloride on the acid ammonium salt. The obtained crystals of the chloride; and from its ability to form chloro-ether, of the general formula,

$$C_6H_4 \begin{cases} CO_2R \\ SO_2Cl, \end{cases}$$

in which the chlorine could be easily replaced by hydroxyl forming an acid of the structure, $C_6H_4 \begin{cases} CO_2R \\ SO_2OH, \end{cases}$ they represented its structure by the formula,

$$C_6H_4 \begin{cases} CO\,Cl \\ SO_2Cl. \end{cases}$$

No evidence was obtained that this chloride was not homogeneous.

Remsen and Coates (3), in 1891, studied this action of aniline on the chloride, and obtained two isomeric anilides quite different in properties, and an anil. From this work it seemed

(1) American Chemical Journal 1, [illegible]
(2) Ibid, 11, 532.
(3) Ibid, 13, 217.

quite evident that there were two isomeric chlorides, from which the anilides were derived.

Later Remsen and Kohler (1) obtained one of these chlorides pure, in crystalline form, while the other one was an oil, always containing more or less of the crystalline variety. It was further shown in this investigation that the anil and the fusible anilide described by Remsen and Coates (2), were derivatives of the symmetrical (or solid) chloride, $C_4H_5\begin{matrix}CoCl\\SoCl\end{matrix}$, while from the unsymmetrical or liquid chloride, for which the formula $C_6H_4\begin{matrix}CCl_2\\SO_2\end{matrix}>O$ had been proposed, the infusible anilide, together with some of the fusible one, was obtained.- The liquid chloride was first obtained pure by Remsen and Saunders (3), who obtained it as thin white needles, by crystallizing from petroleum ether, b. p. 80°, at low temperatures.- The melting point of this chloride was found to be 21.5°-22.5° uncorr., that of the solid chloride 76°-77° uncorr.-

Mr. S. R. McKee, working in this laboratory, has recently shown that both anilides are formed by the action of aniline on the pure low melting (or liquid) chloride in ether solution.

Remsen and Kohler's work showed that the structure

(1) Am. Ch. Jour. 17, 330.
(2) Loc. Cit.
(3) Ibid. 17, [illegible].

of the fusible anilide is represented by the formula,

$$C_6H_4 \begin{cases} CO\ N\ H\ C_6H_5 \\ SO_2\ N\ H\ C_6H_5 \end{cases}$$

and that of the anil by the formula,

$$C_6H_4 \begin{cases} CO \\ SO_2 \end{cases} > N.\ C_6H_5.$$

The evidence for these formulae is as follows:--

Orthotoluenesulphone chloride with aniline gives a compound of the structure

$$C_6H_4 \begin{cases} CH_3 \\ SO_2\ N\ H\ C_6H_5 \end{cases}$$

on oxidation this passes over to the acid,

$$C_6H_4 \begin{cases} CooH \\ SO_2\ N\ H\ C_6H_5 \end{cases}$$

which with phosphorus pentachloride goes over to the anil, which can hardly have any other structure than that indicated by the formula

$$C_6H_4 \begin{cases} CO \\ SO_2 \end{cases} > N\ C_6H_5.$$

Now this is identical in every particular with that obtained from the solid chloride, and when boiled with aniline it goes over into the anilide derived from that chloride, which therefore has the formula $C_6H_4 \begin{cases} CO.\ N\ H\ C_6H_5 \\ SO_2.\ N\ H\ C_6H_5 \end{cases}$.

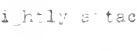
It follows therefore that, in all probability, this chloride

as [illegible] indicated by the formula

The work of Remsen and Saunders (1) adduces additional evidence that this is the correct formula for this chloride.-

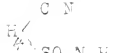
When concentrated ammonia is shaken with the mixed chlorides, the liquid chloride is readily decomposed, the solid chloride being but slightly attacked. Mr. A. D. Chambers of this laboratory, found that the product formed from the liquid chloride was ammonium orthocyan-benzenesulphonate,

Mr. McKee has found that the pure liquid chloride forms the same compound, together with a small quantity of saccharane. It is difficult to understand the formation of this cyansulphonic acid under these conditions, except on the assumption of the formula



for the liquid chloride.

If this be the correct formula for this chloride, the formula of the anilide derived from it follows, and may be written thus:-



(1) Loc.Cit.

Remsen and [illegible] (1) [illegible] t [illegible] [illegible] [illegible] lide was [illegible] easily stable [illegible] towards reagents. The first evidence obtained which indicated that there had no [illegible] deep-seated change in the arrangement of the constituent elements was from the reaction between it and benzoyl chloride, [illegible] which benzanilide was formed.--The other products of this reaction were not isolated.

The further ascertained that this anilide was acted on by phosphorus oxychloride, and by phosphorus pentachloride, though the products formed were not studied.

It was primarily with the hope of being able to clear up the nature of these reactions that this investigation was begun.-- The results arrived at are given below.-- For convenience the chlorides are spoken of as solid and liquid respectively, and the anilides as fusible and infusible.

(1) Loc. cit

## II. PREPARATION OF MATERIAL.

As the method now in use, devised by Mr. E. R. McKee, differs somewhat from that heretofore described for preparing the chlorides, it is given in detail. The dry acid potassium salt prepared from commercial saccharure is mixed, in finely powdered condition, with phosphorus pentachloride, in the ratio of one molecule of the salt to two and a half molecules of the pentachloride. After the action has ceased, the phosphorus oxychloride is distilled off under diminished pressure, or in open dish on the water bath.- The oily residue is then washed two or three times with cold water, by thoroughly agitating the mixture, in a wide-mouthed glass cylinder, with a conveniently bent glass rod.-- The oily chlorides, as free from water as possible, are then transferred to a beaker, placed in a freezing-mixture, and constantly stirred till the oil has solidified. The stirring is necessary to prevent the solidifying mass from adhering to the beaker.- In this solid condition, it is ground fine in a previously cooled mortar, transferred to a filter, and washed entirely free from the acid.

phosphorus by use of ice water.-

If care be taken to avoid contact with [illegible], the chlorides may be pressed almost completely dry between folds of filter paper.- They should be kept in a desiccator till required for use.-

## III. THE ACTION OF WATER ON THE MIXED CHLORIDES.

Remsen and Saunders (1) found that both chlorides were decomposed by water, forming the free acid together with hydrochloric acid, but noted no difference in the rate of decomposition for the two substances.- To test this point, 2 grams of the mixed chlorides were placed in 150cc cold water, and allowed to stand at the temperature of the room for 17 days, being thoroughly shaken from day to day.- The insoluble residue was then filtered off, washed with cold water, and carefully dried.- It weighed 0.41 gram, and, without crystallizing, gave a melting point of 74°-75° uncorr.- Hence it was almost the pure solid chloride.-

(1) A. C. J. [illegible]

## IV. THE ACTION OF ANILINE ON THE CHLORIDES.

As already mentioned, Remsen and Coates, and later Remsen and Korler also, studied the action of aniline on the mixed chlorides, and described the products formed.-- Thinking one of the chlorides might be more readily acted on than the other, the following experiments were made, with the results noted below.-

1st.--To a weighed quantity of the chlorides in 100 cc of water was added aniline in the ratio of one molecule aniline to one of the chlorides.- After standing for 24 hours, with frequent shaking, crystals of each of the two anilides were obtained from the products formed, and some of the mixed chlorides had not been decomposed.- Aniline hydrochloride was also formed.

2nd.--In this experiment the ratio of the aniline to the chlorides was two molecules of the former to one of the latter, and the temperature of the water was kept at zero for the first three hours after mixing the compounds.- Besides aniline hydrochloride, both anilides were formed, and some of the solid chloride was still unacted on.- But from this experiment

with ether as the chlorides, above described, the presence of the solid chloride only may have been due to the fact that the liquid chloride, not acted on by the aniline, had been decomposed by the water, as the products formed remained in the water for 5 days before being examined.-

3rd.-The chlorides were next treated with aniline in the ratio of four molecules of the latter to one of the former, but ether was used as the menstruum, in place of water. Much heat was given out during the reaction, the ether was kept cool by means of cold water.- The products formed were the two anilides and aniline hydrochloride. Chloroform and benzene were tried as solvents in which to effect the reaction, the relative quantities of the aniline and the chlorides being the same as with ether as the solvent.- In each case the products formed were the same as when ether was used.-

As the yield seemed better when these solvents were used than when the two compounds were brought together and dissolved in water, the use of the ether was adopted for preparing the anilides used in the investigation.- The method used is given in detail.-

[illegible] grams of the mixed [illegible] dissolved in [illegible] [illegible] 200cc Erlenmeyer [illegible]; 58.5 [illegible] aniline, also in solution in absolute ether, are added slowly to the chlorides, the solution being constantly stirred. The temperature of the solution is to be kept down by placing the flask in cold water.- A white precipitate appears as soon as the aniline is added. When the reaction is over, the ether is distilled off on the water bath, but this does not proceed smoothly, owing to the insoluble products of the reaction. To avoid bumping, the flask should be shaken constantly while the distillation proceeds. Even then bumping is not entirely avoided.-

The yellowish-white residue contains the mixture of the two anilides with aniline hydrochloride. Sometimes the residue has an oily appearance, and usually contains a slight excess of aniline. Cold water acidulated with hydrochloric acid is then added, the residue thoroughly stirred, and allowed to stand several hours. This treatment removes the aniline salts, and leaves the mixture of the two anilides.- Some of the infusible anilide will be dissolved in the water with the salts of aniline, hence this should be recovered by evapora-

[illegible] anilide will crystallize, leaving the anilide hydrochloride in solution. This anilide is quite frequently colored, but may be purified by boiling with animal charcoal in dilute alkaline solution.

To separate the two anilides the following method [illegible]: The mixture is dissolved in hot alcohol, and this solution is cooled as rapidly as possible by cutting the vessel in cold water. Under these conditions the fusible anilide crystallizes in thin white needles, while the [illegible] variety always crystallizes as short thick prisms. By rotating the vessel the fusible anilide will be disseminated through the alcohol, and may be poured off from the infusible prisms which will quickly settle to the bottom.

By proceeding as above described there is usually [illegible] small amount of the anil, and sometimes a considerable [illegible] of it appears. Since this is insoluble in cold dilute solution of sodium hydro~~chloride~~, while the anilides are soluble in that reagent, the latter may be readily [illegible] from the former by that means.

If the molecule of alcohol with which the infusible anilide crystallizes [illegible] solution in alcohol is undesirable,

[illegible] is [illegible] of sodium hydrochloride, and the solution acidified, [illegible] anilide will [illegible] without water or alcohol [illegible] distillation.

## V. ACTION OF PHOSPHORUS OXYCHLORIDE.

1. On the Infusible Anilide.- Remsen and Kohler (1) observed that phosphorus oxychloride acted on the infusible anilide, but none of the products were isolated.

Since phosphorus oxychloride attacks rubber or cork stoppers, the following expedient was resorted to:- A small condenser was fitted over the neck of a tubulated retort. Such an apparatus may be used for regular distillation, or where a return condenser is desired, as was the case in this experiment. The infusible anilide is then boiled with an excess of the oxychloride, until all the anilide is dissolved. This is attended by liberation of hydrochloric acid, and the solution becomes quite yellow. When the reaction is complete, the excess of the oxychloride is removed by distillation under diminished pressure. There is left in the retort a light brown viscous liquid.- While still warm the retort is turned

(1) Am. Chem. Jour. XVII, [illegible].

about, so [illegible] is a [illegible] is [illegible] over [illegible] much [illegible] as possible. Water is then added [illegible] the return [illegible] until the brown viscous mass has disappeared. [illegible] insoluble almost white material, which dissolves in hot alcohol, forming a yellow solution. After repeated crystallization, it melts sharply at 189.5° uncorr. An [illegible] this product gave the following results:-

I. 0.2009 gram gave 0.4907 gram $CO_2$ and 0.078 gram $H_2O$.

II. 0.2015 gram gave 0.5020 gram $CO_2$ and 0.0795 gram $H_2O$.

III. 0.2143 gram gave 0.1[illegible]5 gram $BaSO_4$.

IV. 0.1683 gram gave 0.1132 gram $BaSO_4$.

| Calculated for $C_{[illegible]}H_{[illegible]}N_2SO_2$ | | Found. I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|---|
| C | 68.[illegible] | 68.07 | [illegible].05 | - - | - - | - - | - | - |
| H | [illegible].20 | 4.33 | 4.[illegible] | - | - | - - | - | |
| S | [illegible].53 | - | - | 9.24 | 9.25 | - - | - - | |
| N | 8.41 | - | - | - - | - | 8.63 | 8.61 | 8.[illegible] |

The combustions [illegible] [illegible], as described by [illegible] R[illegible]), [illegible]

(1) Am. [illegible], XII, [illegible].

[illegible] made [illegible] (VII), [illegible], E. McKay, [illegible] [illegible] of Kjeldahl.-

Considerable difficulty [illegible] in [illegible] satisfactory results for carbon, [illegible] the [illegible] and the melting point of the compound indicated its purity. After [illegible] a possible explanation was found in the fact that some of the anal described by Remsen and Coates (1), [illegible] found [illegible] result under the conditions of the experiment. Its formation will be explained below.-

When pure this compound is of bright lemon-yellow color, and the crystals obtained from alcohol are beautifully formed arborescent plates, very brittle. It is only slightly soluble in ether, or chloroform, readily soluble in benzene, glacial acetic acid, and acetone.- When crystallized from either of the last two solvents named, monoclinic prisms of great brilliancy are obtained, the faces developed being usually $\alpha\alpha$, $\alpha P\bar{\alpha}$, $\alpha P$, P, and $2P\alpha$.-

2. On the Fusible Anilide. This same compound [illegible] [illegible] of [illegible] oxychloride on the fusible anilide, the details of the experiment being the same as with

(1) Am. [illegible]

VI. THE ACTION OF PHOTO[illegible] OXIDES.

with [illegible] chloride, [illegible] reaction [illegible] be [illegible],

$$R\left\langle\begin{matrix} C\ O\ N\ R' \\ C\ O\ O\ H \end{matrix}\right. + CH_3\,CO\,Cl = R\left\langle\begin{matrix} C\left\langle\begin{matrix} N\text{-}R' \\ OH \end{matrix}\right. \\ COO\ H \end{matrix}\right. + CH_3\,CO\,Cl$$

$$R\left\langle\begin{matrix} C= \\ \quad\ \ \diagdown O \\ CO \end{matrix}\right. + CH_3\,C\,O\,O\,H + H\,Cl.$$

(Isoimides)

[illegible] the oxychloride the (Isoimides) reaction would be [illegible] gous.- In all cases examined, $\underline{R'}$ was $CH_3$, $C_2H_5$, or $C_6H_5CH_2$, while $\underline{R}$ was the residue of camphoric, and phthalic acids respectively. Clearly the role of the oxychloride in these reactions was the same as that which it plays in the reaction with the anilides. The equation,

$$3\,C_6H_4\left\langle\begin{matrix} CO\ N\ H\ C_6H_5- \\ SO_2\ N\ H\ C_6H_5- \end{matrix}\right. + P\,O\,Cl_3 = 3\,C_6H_4\left\langle\begin{matrix} C= \\ \quad\ \ \diagdown N.\ C_6H_5 \\ SO \end{matrix}\right. + H_3\,P\,O_4 + 3\,H\,Cl,$$

then represents the reaction with the fusible anilides.

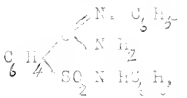
3. Structure of this Compound.- From the [illegible] formation already described, especially those involving [illegible] use of the fusible anilide, the formula for which is entirely satisfactorily represented as above, it naturally follows that the formula,

$$C_6H_4\left\langle\begin{matrix} C= \\ \quad\ \ \diagdown N.\ C_6H_5 \\ SO_2 \end{matrix}\right. N.\ C\ H\ ,$$

[illegible] It [illegible]

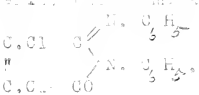
[illegible] anil of [illegible] thiosulphonic acid.

Jespr[illegible] (1) obtained this same [illegible] [illegible] anilin[illegible] [illegible] chloride. [illegible] the first [illegible] is a [illegible] a [illegible],

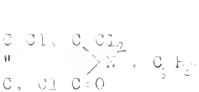


[illegible] that [illegible] forming [illegible] anil, [illegible] gives [illegible] structural formula as [illegible] designed.-

[illegible] two aniline residues in [illegible] anil is [illegible] same as that given by Abschütz and Jeavis (2) [illegible] dichloroalcic-diazil, [illegible] of which is,



which is formed by the action of aniline on [illegible] anil dichloride,



prepared [illegible] action of [illegible] anil (3).

(1) Ber. [illegible]
(2) Ber. [illegible]
(3) Ann. [illegible]

It seems [illegible] the analogous derivative of [illegible] Coates. Preliminary experiments have been [illegible] with this end in view, but as yet without success. The matter [illegible] under investigation.-

[illegible]. Chemical Properties of the Dianil.- (a) It was mentioned above that this compound may be crystallized from glacial acetic acid.- For this purpose the solution must not be heated longer than is necessary to effect solution. If the solution be boiled for two or three hours in a flask connected with a reflux condenser, none of the dianil will separate on cooling, but instead there will appear slender white needles.- These are crystals of the infusible anilide. The identity was established by the melting point, crystalline [illegible] when recrystallized from alcohol, and from water, ready solubility in dilute cold alkaline solution, from which the characteristic granular crystals of the infusible anilide separate when the solution is acidified. The infusible anilide itself assumes the acicular habit if crystallized from glacial acetic acid.- To further test the identity some of these needles were treated with phosphorus oxychloride, and [illegible], with

[illegible] [illegible] [illegible] [illegible]

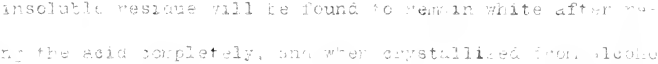
[illegible] [illegible] [illegible] [illegible]

[illegible] [illegible] [illegible] [illegible]

these elements [illegible] in the more stable [illegible] of the infusible, rather than the fusible anilide, which is less stable.

(c) When concentrated hydrochloric acid is added to the dianil, the ~~yellow~~ color of the latter changes from yellow to white. If the acid be filtered off at once, and the residue washed with cold water, the yellow color reappears. If, however, the dianil be boiled with the acid for about an hour, the insoluble residue will be found to remain white after removing the acid completely, and when crystallized from alcohol, it forms slender white needles. These are crystals of the anil described by Remsen and Coates (1). In the hydrochloric acid solution is some aniline hydrochloride. This reaction may be represented by the equation,

$$C_6H_4\left\langle\begin{matrix} C \\ SO_2 \end{matrix}\right\rangle\begin{matrix} N.C_6H_5 \\ N.C_6H_5 \end{matrix} + H_2O + HCl = C_6H_4\left\langle\begin{matrix} CO \\ SO_2 \end{matrix}\right\rangle N.C_6H_5 + C_6H_5NH_2.HCl.$$



It was mentioned above that some of this anil was always formed during the action of phosphorus oxychloride on the anilides. In the light of the above reaction, its presence is explained, being a secondary reaction between the dianil and the hydrochloric acid liberated during the reaction.

(1) Loc. Cit.

## VII. ACTION OF PHOSPHORUS PENTACHLORIDE ON THE INFUSIBLE ANILIDE.

When the infusible anilide is [illegible] to a [illegible] solution of phosphorus pentachloride in [illegible] reaction sets in at once, [illegible] generally the solution [illegible] to a light yellow in color. Usually about twice as [illegible] pentachloride as of the anilide is necessary to effect complete solution of the latter. In the first experiment tried, [illegible] grams of the pentachloride were used to one gram of the anilide, and the heating was continued only as long as was necessary to effect complete solution of the anilide. On cooling, radiating tufts of fine white needles separated, completely filling the liquid. More chloroform was added and heat applied till all the needles were dissolved. But the needles did not separate again, even when almost all the chloroform had evaporated. The last traces of chloroform were then driven [illegible] [illegible] for some time, and the yellow viscous [illegible] was treated as the brown residue [illegible] the oxychloride experiment [illegible]. Some of the anil was found present, though the chief product was the yellow dianil. The [illegible] products [illegible] reaction

are the same as those [illegible] by the action of [illegible] chloride on the infusible anilide.-

This experiment was [illegible] the same condition as before and under varied conditions, though [illegible] without obtaining those fine white needles. The final products were the same each time.

From the results of the experiments it will readily be seen that it is possible to pass from the fusible anilide to the infusible anilide, by passing first to the [illegible] anil, and then, boiling this with glacial acetic acid, or alcoholic solution of potassium hydroxide, to the infusible anilide.

Again, from this dianil one may obtain the anil by boiling with concentrated hydrochloric acid. And since the anil, when boiled with anilide, passes over to the fusible anilide, it is therefore possible to pass in the opposite direction, from the infusible to the fusible.

VIII.-THE ACTION OF BENZOYL CHLORIDE ON THE INFUSIBLE ANILIDE.-

Five grams infusible anilide were boiled with an excess of benzoyl chloride until it had dissolved. The excess

of the benzoyl chloride was removed completely in [illegible], by distillation under diminished pressure, and the residue boiled with water. After this water had become cold, and without separating it from the insoluble residue, sodium carbonate was added to alkaline reaction, and the vessel was heated gently on the water-bath to about 70° C.- This solution was then poured off from the undissolved residue, and acidified when benzoic acid was precipitated.-

The residue insoluble in sodium carbonate solution was then dissolved in alcohol, and boiled with animal charcoal. From this solution separated plates of a dirty-yellow color, but which when purified by repeated recrystallization, became white, and assumed the acidular habit, melting sharply at 190.5° uncorr. They proved to be the anil.-

The mother liquor from the above was then evaporated to dryness, and the residue boiled with about 750 c.c. water, and the water while still hot was siphoned from the part insoluble in the water, which had melted to a brown oil. [illegible] repeatedly boiling this residue with water almost all [illegible] [illegible] dissolved.

From this [illegible], [illegible] [illegible] precipitate

deposited.- When crystallized from alcohol, it forms small globular shaped tufts of white needles, but these have not yet been identified, partly from lack of material, partly from lack of time.

From the water filtrate from this white precipitate, after evaporating to a very small volume, a small quantity of phenanilide was obtained, which was identified by its melting point, crystal form, and by comparison with a specimen of benzanilide.- The equation

represents the reaction as far as yet understood.-

A second experiment gave the same results as the one just described.- No trace of the product mentioned by Remsen and Kohler (1), as giving rise to the infusible anilide on addition of aniline, was obtained in either case.- It is possible that this product might be isolated by keeping the temperature as low as possible in order to effect the reaction.

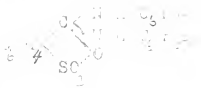
STRUCTURE OF THE INFUSIBLE ANILIDE.

From the results obtained in this investigation, it

(1) Am. Chem. J., 17, 31.

[illegible]

[illegible] is [illegible] aniline by [illegible] represented [illegible]



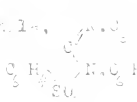
first [illegible] Hessler and Costanzo(1)

## IX.- CONCLUSION.

[illegible]

1. Water [illegible] the liquid chloride [illegible] the solid chloride.

2. Ortho [illegible] anil, having the structure represented [illegible] formula,



is obtained [illegible] action of phosphorus oxychloride [illegible] phosphorus [illegible] on either aniline [illegible]

[illegible]

[illegible] [illegible] [illegible] [

BIOGRAPHICAL.

[redacted] was born near Apex, Wake Co., N. C., June 4th, 1868. His early education was received in private schools in that village. He entered Wake Forrest College, N. C. September, 1881, receiving the degree of Bachelor of Arts in 1885. For three succeeding years he taught in private schools in his native State. He returned to Wake Forrest College September, 1888, and received the Master's degree in 1889. In October of that year he entered the Johns Hopkins University, remaining two years. During the two years 1891-93, he taught in the Wisconsin State Normal School, located at Oshkosh.- Since October, 1893, he has continued his work at the Hopkins University. His subjects have been Chemistry, Mineralogy and Physics.